

JADWIGA PROKSA^{1*}, MARIAN JACEK ŁĄCZNY¹, ZBIGNIEW BZOWSKI¹**EVALUATION OF THE POSSIBILITY OF USING GRANULATED CARBONATED
VOLATILE FLY ASH FROM FLUIDIZED BEDS (G-CVFA)
IN UNDERGROUND MINING TECHNIQUES**

The application of fluidized fly ash in underground mining excavations is limited due to its significant content of free calcium and calcium sulfate. In order to increase the amount of utilized fly ash from fluidized beds, it should be converted to a product with properties that meet the requirements for mining applications. This research presents the results of an attempt to adapt fluidized fly ashes for use in underground mining techniques, by means of carbonation and granulation. Carbonation was performed with the use of technical carbon dioxide and resulted in the reduction of free calcium content to a value below 1%. Granulation on the other hand, resulted in obtaining a product with good physical and mechanical parameters. The performed mineralogical and chemical studies indicate that trace amounts of “binding” phases, such as basanite and/or gypsum are present in the carbonized ash. The addition of water, during the granulation of carbonized fluidized fly ash, resulted in changes in the mineral phases leading to the formation of ettringite and gypsum as well as the recrystallization of the amorphous substance. It was confirmed that the carbonization and granulation of flying fluidized ashes positively affects the possibility of using these ashes in underground mining excavations.

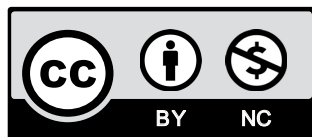
Keywords: fluidized fly ash, underground mining techniques, carbonation, granulation

1. Introduction

The introduction of energy blocks, which work on the basis of fluidized bed boilers, raised a problem of managing the emerging bottom and fly ashes due to their different physical and chemical properties in relation to ashes generated in traditional pulverized boilers. The main cause of these differences is the temperature of coal combustion; in pulverized boilers it is ap-

¹ CENTRAL MINING INSTITUTE, 1 GWARKÓW SQ., 40-166 KATOWICE, POLAND

* Corresponding author: jproksa@gig.eu



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proximately 1300°C, while in fluidized bed boilers it is approximately 950°C. Another reason is the addition of limestone as a sulfur dioxide binding sorbent.

It is estimated that about 4.2 million tons of volatile fluidized ash (VFA) is produced in Poland annually (Stoch, 2015; Wójcik et al., 2017). So far, this ash is used mainly in construction, land reclamation works, cement plants and mining. The utility of these ashes in all of the aforementioned cases is limited due to the presence of free calcium and sulfates.

The chemical composition of these ashes, used simultaneously for carbonation are shown in Table 1.

TABLE 1

Chemical composition of volatile fluidized ashes before (VFA) and after carbonation (CVFA)

Component	VFA	CVFA
	in %	
SiO ₂	39.22	37.88
TiO ₂	0.48	0.44
Al ₂ O ₃	18.30	17.12
Fe ₂ O ₃	4.50	4.47
CaO	21.50	22.80
MgO	1.02	1.14
Na ₂ O	0.24	0.30
K ₂ O	1.19	1.22
P ₂ O ₅	0.05	0.05
SO ₃	10.87	8.90
Calcination losses	2.15	5.25
Sum	99.52	99.57

In PN-EN 450-1: 2012, sixteen chemical parameters have been determined that fly ash should fulfill in order to be used for the production of concrete, clinker and cement, as well as for road foundations and building ceramics. The most important are: free calcium oxide, reactive calcium oxide and sulfate content, as well as the total amount of silicon, aluminum and iron oxides. In the case of using fluidized fly ash for work in underground mining excavations, free lime and calcium sulfate content should be considered crucial parameters.

These restrictions do not pose a problem if fly ashes are used to seal gobbs. However, only part of all waste generated may be utilized with this application of VFA. The question then arises concerning whether converting VFAs into a product with properties that meet the requirements for use in mining (such as: the limitation of the leaching of harmful substances or the durability of a solidified structure) is a way to increase their applicability. It appears that the granulation technique, commonly used to agglomerate dusty substances, can create such a possibility (Klassien & Griszajew, 1989).

Granulation is used to obtain a convenient form of the final product and to facilitate its application in appropriate technologies (Heim, 2012).

The literature on the subject shows that ash granulation is often used with a view to new directions of application (Szczygielski, 2017; Ohnaka et al., 2005). The basic research directions are focused on, for example, the use of various binding materials to improve product properties in line with the expectations of recipients (Gomathi, 2015; Augusta, 2017; Bogdanov, 2012).

From the cited literature, it is clear that non-pressure granulation applies to the granulation of fly ash. In this process, intensive mixing of the material particles takes place, and under the influence of external forces and forces of mutual pressure, they are joined together, gradually compacting and increasing the forming agglomerates. The mechanism of grain formation in the granulation process consists of the joining of particles by means of liquid bridges. The surface tension forces of the granulation liquid and the capillary forces contribute to the joining of the particles. As a result of these forces, a granule with a certain cohesion and durability can be created (Klassien & Griszajew, 1989).

The presented research assumes that granulation can be useful as a method for processing ashes into a new type of product, especially when combined with the simultaneous neutralization of free calcium oxide and using calcium sulfate as an additional binding agent. Such an approach can create new opportunities for increasing their use in mining.

The research presents the results of an attempt to adapt fluidized fly ashes for use in underground mining techniques, by means of carbonation and granulation. Carbonation was performed with the use of technical carbon dioxide and resulted in the reduction of free calcium content to a value below 1% (Łączny et al., 2015). The adopted research thesis assumed that in carbonated fluidized fly ash (CVFA), phase transformation of anhydrite, leading to the formation of gypsum (Łączny & Bzowski, 2017), may be beneficial for its use in underground mining techniques. The presence of calcium carbonate and calcium sulfate in an appropriate proportion has a beneficial effect on the formation of ettringite and calcium aluminates (Kurdowski, 2010), and at the same time can reduce the risk of changes in the durability of ash granules as a result of the formation of the “secondary ettringite”. The incubation period of ettringite in solidified fluidized ashes usually ends after seven days from the time of water addition (Rajczyk, 2012), which seems to be a favorable indicator from the point of view of the use of granules in mining technologies.

2. Material and methods

The study was carried out with the use 10 kg of fly ash from the fluidized bed of Łągisza Power Plant, which was subjected to carbonation in the manner described in the paper (Łączny et al., 2015) and in the patent PL 410867. As a result, carbonated volatile fluidized ash (CVFA) was obtained.

After obtaining CVFA with a satisfactory content of free calcium oxide (0.1%), a simultaneous three-phase granulation process was carried out in the system: solid – liquid – gas in a granulator (Intensive counter-rotary mixer manufactured by IdeaPro to order Department of Material Engineering Central Mining Institute), presented in Fig. 1. Operating parameters of the granulator during the experiment: height of rotor rotation 600-800 rpm, bowl rotation height 40-60 rpm, granulation time was about 130 min and volume of the mixing chamber as well as weight 1200 dm³.

The method of operation of an intensive counter-rotary mixer involves intensive mixing of the mass, located within the range of a high-speed rotor rotating in the direction opposite to the direction of the rotation of the mixing bowl (Morsch, 2005). The mixing bowl of the agitator is inclined with respect to the horizontal level and provides the mixture to the areas where mixing tools operate. The movement of the mixing tool allows the creation of the concurrent or countercurrent flow of mixed material with large differences in velocity in individual layers moving relative to each other. The stationary scraper is a permanent, vertical element shaping the flow of the mixture, which reliably prevents the formation of accretions and dead zones (Korol & Serkowski, 2005).

The movement of the material in an intense counter-rotary mixer and its construction results in the uniform distribution of the additive (i.e. water) and granulation, which ensures that each grain has a homogeneous composition in its entire volume (Fig. 2). Water is necessary both for the initiation of the carbonation process, enabling the reaction of free calcium oxide present in the ash with carbon dioxide gas, and for the granulation process in which it activates the surface bonds of the granules causing their gradual growth. Granulation in such a granulator-mixer results in the formation of dense granules, therefore a compacted and simultaneously agglomerated material with the desired shape and dimensions is obtained (Korol & Serkowski, 2005). The optimal duration of the process, as well as the appropriate speed of the rotor and agitator bowl were established experimentally. The granulator's workspace was supplied with 100% carbon dioxide. A constant inflow of carbon dioxide in the amount of approximately $2 \text{ dm}^3/\text{min}$ was maintained during the whole process. The obtained material was then homogenized with the addition of water and subjected to a pelletizing process to obtain granulated carbonated volatile

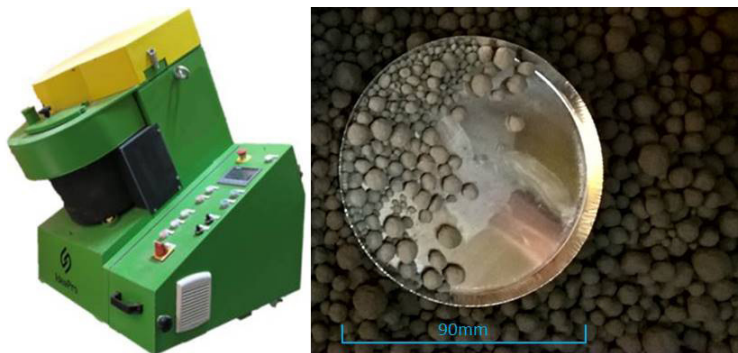


Fig. 1. Intensive counter-rotary mixer manufactured by IdeaPro to order Department of Material Engineering Central Mining Institute; obtained granulated carbonated volatile fluidized ash

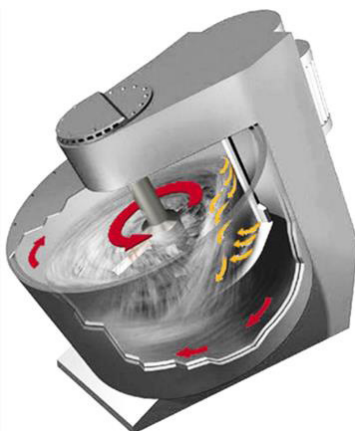


Fig. 2. Movement directions of the processed material inside the intense counter-rotary mixer during its operation

fluidized ash (G-CVFA) (Fig. 1). As mentioned earlier, the device enables the homogenization, carbonation and granulation process during one technological operation. It enables granulates with a very high degree of homogeneity of fine-grained substances to be obtained.

The created product of granulation is characterized by low strength parameters. The G-CVFA obtained was subjected to seasoning under dry-air conditions for a period of 28 days (this time was arbitrarily adopted based on the cement mortar strength test), in order to increase its strength. Then, tests of the products resistance to crushing were carried out in accordance with the requirements of PN-EN 13055:2016-07. The tests were carried out on a hydraulic press. The material was also subjected to sieve analysis, chemical analysis, X-ray analysis and tests for leachability of some components which are important from the point of the environmental impact of mine waters.

The mineralogical studies of VFA, CVFA and G-CVFA were carried out using the X-ray powder method (DSH) with Bragg-Brentano geometry (using the Bruker D8 Discover Diffractometer in the Central Mining Institute's Department of Environmental Monitoring), CuK α radiation, Ni filter and LYNXEYE_XE detector. Mineral composition was determined and calculated on the basis of standards licensed in PDF-4 + 2018 RDB based on the ICDD (International Center for Diffraction Data) and databases: the ICSD (Inorganic Crystal Structure Database) and the NIST (National Institute of Standard and Technology). DIFFRAC v.4.2 and TOPAS v.4.2 Bruker AXS were used for registration and diagnostics. Quantitative calculations of crystalline phases were based on the Rietveld methodology (Albinami & Willis, 1982; Bish & Post, 1993; Mahieux et al., 2010; Kowalska, 2013), while the content of amorphous substance was calculated using ZnO as an internal standard.

Chemical studies of VFA and CVFA were performed by X-ray dispersion (XRF) fluorescence spectrometry. The XRF Primus 2 by the Rigaku Corporation was used in the tests at the Department of Environmental Monitoring of the Central Mining Institute in Katowice.

3. Results

3.1. Granulation

For the obtained granulated carbonated volatile fluidized ash samples, grain size analysis was performed by sieve analysis and the results are shown in Table 2.

TABLE 2

Grain size analysis of granulated ash

Grain size fraction, mm	Share amount, %
>10	0.2
8-10	1.5
6-8	5.7
4-6	29.8
2-4	48.6
1-2	8.7
0.5-1	0.9
-0.5	4.2
<0.1	0.4

Through analysis of the obtained results, it can be concluded that approximately 80% of the population are granules with diameters between 2 and 6 mm, with a the greatest amount being between 2-4 mm. The obtained material is therefore fairly homogeneous.

3.2. Test of resistance to crushing and compressibility

The aim of the strength tests was to determine the granulated carbonated fluidized ash's (G-CVFA) resistance to crushing. The product was tested in accordance with PN-EN 13055: 2016-07. The compressibility test was carried out in accordance with PN-93/G-11010. According to the quoted standard, the tests for crushing resistance can be carried out for aggregates with a grain size in the range of 4-22 mm and bulk density greater than 150 kg/m³. Therefore, prepared samples of G-CVFA (with a bulk density of 860 kg/m³ according to the standard PN-EN 1097-3) were deprived of those with a grain size below 4 mm, and then placed in a steel cylinder (Fig. 3) and vibrated in order to condense it. The piston was then pressed into the cylinder to a certain depth and placed in the hydraulic press, where the working force plunged the piston to the specified depth in a specified time. The test was repeated for three material samples. The average value for G-CPLF was 4.8 MPa. Compressibility at a pressure of 15 MPa was 36.4%.



Fig. 3. Test of resistance to crushing

3.3. Physical and mechanical properties

For samples of granulated carbonated fluidized ash, the determination of washability, water permeability, and leaching tests were carried out according to the standard PN-EN 12457-4:2006.

TABLE 3

Physical properties of granulized carbonated volatile fluidized ash

Property	Unit	G-CVFA after 7 days of contact with underground waters (mining)
Washability	%	9.9
Water permeability	m/s	$4.8 \cdot 10^{-4}$
pH of water extract	%	10.5

3.4. Mineralogical and chemical composition

The mineral composition of the samples tested is presented in Table 4.

TABLE 4

The mineral composition of the test samples

Component	Volatile fluidized ash (VFA)	Carbonation volatile fluidized ash (CVFA)	Granulized carbonation volatile fluidized ash (G-CVFA)
	Contents in %		
Anhydrite (CaSO ₄)	23.0	22.0	20.0
Quartz (SiO ₂)	20.5	17.5	17.5
Feldspar (potassium* + plagioclase**)	2.0	2.0	3.0
Muscovite (KA ₁ [AlSi ₃ O ₁₀ (OH) ₂])	2.0	2.0	2.0
Hematite (Fe ₂ O ₃)	2.0	2.0	2.0
Mullite (3Al ₂ O ₃ · 2SiO ₂)	2.0	2.0	2.0
Magnetite (FeFe ₂ O ₄)	1.0	1.0	1.0
Substance CaO	3.0	—	—
Substance CaSO ₃	1.0	—	—
Calcite CaCO ₃	0.5	5.5	6.5
Portlandite (Ca(OH) ₂)	—	2.0	—
Bassanite (CaSO ₄ · 0,5H ₂ O)	—	—	2.0
Substance Ca ₆ Fe ₂ (SO ₄) ₃ (OH) ₁₂ · nH ₂ O	—	—	2.0
Gypsum (CaSO ₄ · 2H ₂ O)	—	—	1.0
Amorphous substance	42.5	43.5	40.5

The differences in the amount of components, such as CaO, calcite (CaCO₃) and quartz (SiO₂), between volatile fluidized ash (VFA) and carbonation volatile fluidized ash (CVFA) are evident. On the other hand, a constant amount of minerals, e.g. feldspar, muscovite, hematite and magnetite is confirmed regardless of the state of the fluidized ash. The presence of portlandite (Ca(OH)₂) in carbonation volatile fluidized ash (CVFA) results from the hydration of free lime (CaO), which intensively reacts with CO₂ to form calcite. Differences in the amount of calcite in the examined ashes are shown in Figure 5. These differences are explained by the lack of CaO in the remaining ash (Table 4). In granulized carbonation volatile fluidized ash (G-CVFA), phases such as gypsum, bassanite and substance Ca₆Fe₂(SO₄)₃(OH)₁₂ · nH₂O appear, which likely emerge due to pressure stress occurring during the granule formation stage.

In contrast, the impact of both fresh (surface) and saline groundwater (mine) on the G-CVAF granulate, in addition to the formation of significant amounts of gypsum, causes the degradation of anhydrite through the corrosion of the granulate. In reaction with saline groundwater (mine), G-CVAF exhibits low sorption properties, retaining halite and sulfates in the form of jarosite (Table 5).

The chemical composition of the fluidized ashes tested, generally reflects the previously determined mineral composition of the ashes tested, but the amounts of such components as aluminum, calcium and iron seem to be higher than those resulting from mineralogical evaluation. This is due to the large amount of amorphous substance in the investigated fluidized ashes,

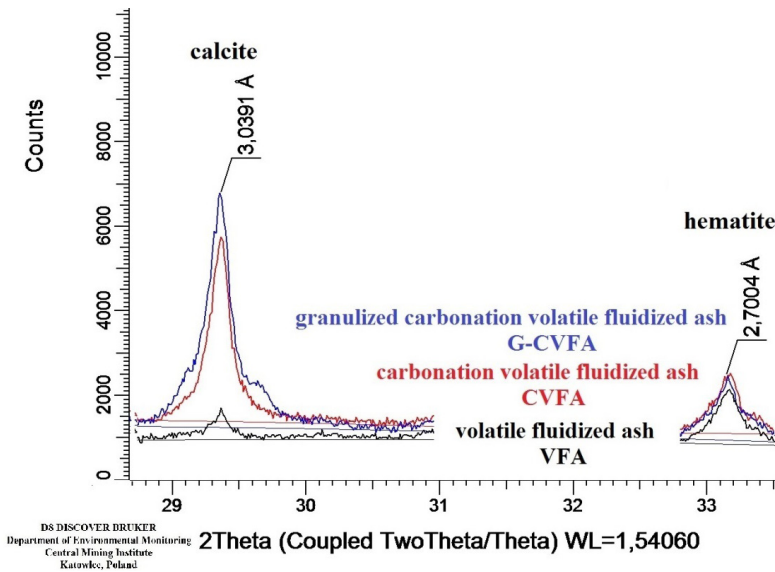


Fig. 4. Determination of calcite and hematite in the tested samples by XRD method

TABLE 5

Mineral composition of G-CVFA after 7 days of contact with water

Component	Granulized carbonation volatile fluidized ash		
	Dry	After 7 days of soaking in water	
		Surface water	Underground mine water
Contents in %			
Anhydrite (CaSO ₄)	20.0	19.0	14.0
Quartz (SiO ₂)	17.5	20.5	18.5
Calcite (CaCO ₃)	6.5	6.5	7.5
Feldspar (potassium* + plagioclase**)	3.0	3.0	3.0
Muscovite (KAl ₂ [AlSi ₃ O ₁₀ (OH) ₂])	2.0	2.0	2.0
Hematite (Fe ₂ O ₃)	2.0	2.0	2.0
Mullite (3Al ₂ O ₃ · 2SiO ₂)	2.0	2.0	2.0
Magnetite (FeFe ₂ O ₄)	1.0	1.0	1.0
Bassanite (CaSO ₄ · 0,5H ₂ O)	2.0	—	—
Substance Ca ₆ Fe ₂ (SO ₄) ₃ (OH) ₁₂ · nH ₂ O	2.0	1,0	—
Gypsum (CaSO ₄ · 2H ₂ O)	1.0	3.0	9.0
Halite (NaCl)	—	—	2.0
Jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆)	—	—	1.0
Amorphous substance	40.5	38.5	37.5

probably consisting of the aforementioned elements and amorphous silica. At the stage of the hydration of fluidized ash, the amount of amorphous substance increases, which may be related to the remaining part of the lime hydrate outside the crystallization of portlandite, in the form

of amorphous $\text{Ca}(\text{OH})_2$. On the other hand, the chemical activity of the components of amorphous substances of the fluidized ash investigated occurs in reactions with water, which results in a decrease in its amount from the range of 40.5-43.3% (Table 4) to 37.5-38.5% (Table 5).

The mineral composition of both analyzed volatile fluidized ashes was predominated by an amorphous substance; among crystalline phase anhydrite, quartz and feldspar dominated. The differences between the fluidized bed ash (VFA) and after (CVFA) carbonation are mainly seen in the amounts of free lime and calcite, which were determined by the XRD method (Fig. 4).

The amorphous substance is formed in various coal combustion zones. In the fluidized bed boilers, the gasification zone and the combustion zone can be clearly distinguished. In addition, desulfurization takes place by adding sorbent to the combustion chamber. The combustion takes place in the temperature range of 750-950°C. Below the temperature of 750°C, the conditions of the oxidation of coal deteriorate and CO is formed. Above 950°C sintering and softening of the ash occurs. The fluidized bed can lose its loose nature and fine-grained structure, taking the form of an amorphous substance, the content of which in the ashes can be up to 40%. This phenomenon may also take place at lower temperatures, especially if there are conditions favourable to creating a reducing environment inside the boiler. An example of the temperature zone distribution in the CFB boiler looks as follows (Kanafek, 2018):

- in the internal circulation zone from approximately 750°C to approximately 960°C,
- in the superheater zone of INTREX from approximately 630°C to approximately 750°C.

Thus, it can be indicated that in the superheater zone of INTREX and in the combustion zone there are conditions approximately analogous to that in the clinker burning process. According to W. Kurdowski (2010), at 800°C to 1000°C, C_{12}A_7 aluminate begins to appear, which then converts into C_3A . In the formulas, the signs used in cement and concrete chemistry were used, where: C stands for Ca, A stands for Al, F stands for Fe, S stands for silica.

After firing the raw material mixture, a product (clinker) is obtained, containing four basic clinker minerals: alit – C_3S – tricalcium silicate, belit – C_2S – dicalcium silicate, C_3A – tricalcium aluminate, braunmillerite – C_4AF – four-calcium aluminum ferrate. Other compounds, which are characteristic for the discussed temperature range, that can form are: CA (at approx. 750°C), $\text{C}_2\text{S} \cdot \text{CaCl}_2$ (between 700°C and 1200°C), $2\text{C}_2\text{S} \cdot \text{CaCO}_3$, $2\text{C}_2\text{S} \cdot \text{CaSO}_4$ (at approx. 950°C), $3\text{C}_2\text{S} \cdot 3\text{CaSO}_4 \cdot \text{CaF}_2$ (above 800°C). The mineral substance of coal also contains small amounts of alkali, sulphates and chlorides that form eutectics with a melting point lower than 700°C. The aforementioned components, although not confirmed to occur in fluidized bed ash, may appear – assumption based on the specific properties of pozzolan ashes (Giergiczny, 2007; Rajczyk, 2012).

4. Discussion

The results of research on the granulation of volatile fluidized ash in a carbon dioxide atmosphere are presented. As indicated in the introduction, the applicability of volatile fly ash depends on their physicochemical properties – mainly the increased content of free calcium and sulphates. The reaction with carbon dioxide in the granulation process favourably changes their chemical and mineralogical composition to the extent that they can be used in mining.

This research was aimed at obtaining a product with increased strength, that could be used in hard coal mining in underground mining techniques. It is possible to granulate VFA without

prior carbonation, however, the product obtained is not stable in the mine water environment. The reason for that is chemical reactions leading to the formation of so-called “external” ettringite. This causes a reduction in strength and the breakdown of the granulate, which is the result of hydration (“slagging”) of free calcium. The prior carbonation of VFA stabilizes the transformation of sulfur compounds and causes ettringite to stay in equilibrium with its other variant containing CO_2 built in to its structure.

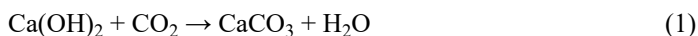
The use of the carbonation process to change fluidized fly ash properties has been proposed in order to obtain a product with controlled content of free calcium oxide (Łączny et al., 2015). This resulted in the production of micro-aggregate, which, as research has shown, can be used as an active ingredient in cement mortars. In addition, the beneficial effect of carbonated fly ash on the strength properties of cement mortar has been demonstrated. (Łączny et al., 2016). Subsequent studies of carbonated fluidized ashes have shown that, due to the beneficial effects of carbonate on the transformation of ettringite, the strength of the mortar made only from these ashes is better when compared to non-carbonated ashes. In addition, the conducted research provided information on the transformation of sulfur compounds during the carbonation of fluidized ashes and showed that not all crystalline phases participate in a complex system of different reactions (Łączny & Bzowski, 2017). The “inert” components of carbonated fluidized ashes include: quartz, feldspar, mullite, magnetite and hematite. Quartz in volatile fluidized ash retains its crystalline structure that prevents reactions with substances containing calcium, as well as permanent feldspar, mullite, hematite and magnetite (Łączny & Bzowski, 2017). In carbonated volatile fluidized bed (CVFA), the free lime reacted to calcite and its final content is below 1%. The free calcium residue is hidden in the form of the fluidized bed grain matrix (Anthony & Granatstein, 2001); the slow destruction of these grains maintains the high pH value of the aqueous extract from CVFA ash. In the case of using carbonated fluidized ashes in underground mining techniques, this phenomenon is disadvantageous due to the risk to people and the aquatic environment of underground workings. In the complex system of chemical reactions occurring during the carbonation of fluidized ashes, compounds containing sulfate ions undergo changes in various ways. The bassanite that appears in the tested solidified ash samples is a precursor to the gypsum crystallization process (Van Driessche et al., 2012). This phenomenon is beneficial for the application of carbonated fluidized ashes in underground mining techniques.

The XRD studies have shown that in the case of granular CVFA, small amounts of “binding” bassanite and/or gypsum (Table 4) are observed. This is due to the lack of the necessary amount of water in the gypsum-ettringite system. The presence of gypsum in the CVFA granulate causes $\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot n\text{H}_2\text{O}$ substance to appear. The amounts of this substance and of bassanite decrease when the G-CVFA has contact with water. In contrast, the interaction of water with G-CVFA results in an increase in gypsum content, from 3 to 9% (Table 5). Longer storage of G-CVFA in water may cause intensification of the gypsum formation process to the amount of approximately 12-15%, which requires confirmation in lysimetric studies and preferably in conditions of underground workings. From the point of view of the potential application of G-CVFA in underground mining techniques, the formation of gypsum is a highly beneficial process, because in addition to bonding, it permanently retains sulfates that therefore do not migrate to groundwater.

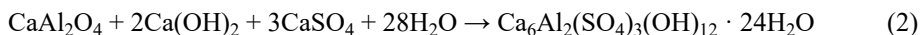
The results indicate that, as a result of simultaneous granulation and carbonation, iron ions (Fe^{3+}) also enter the structure of ettringite. This is probably due to the lower proportion of water added in the granulation process in relation to the amount of water added to the preparation of

ash mortar. The research also showed that in salt water (e.g. mine water) the processes of the hydration of $\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot n\text{H}_2\text{O}$ as well as the crystallization of ettringite, virtually, do not take place. Probably the formation of ettringite in the G-CVAF reaction with water limits the availability of aluminum in the $\text{Ca}^{2+} - \text{Al}^{3+} - \text{SO}_4^{2-} - (\text{OH})^-$ system. On the other hand, the presence of feldspar, muscovite and mullite, found in similar amounts in both carbonated fluidized ash (CVFA) and its granulates (G-CVFA) – also placed in water (Table 5) – indicates that these minerals do not constitute a source of reactive aluminum for the ettringite formation process.

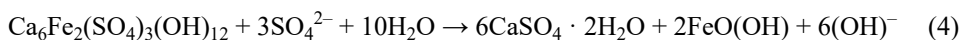
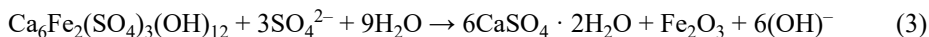
Chemically, the carbonation of fluidized ash leads to the formation of calcite from hydrated free calcium, according to reaction (1).



At the same time, carbonation may be an indirect cause of the formation of other phases associated with the use of $\text{Ca}(\text{OH})_2$. If reactive iron containing substances are available in the amorphous substance of fluidized ashes, it is possible to form the $\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot n\text{H}_2\text{O}$ substance (as found in G-CVFA). The presence of aluminum, $\text{Ca}(\text{OH})$ and anhydrite in a fluidized bed may result in the formation of ettringite (3), but an additional condition is the high availability of water (Kurdowski, 2010). As already stated, the feldspar, muscovite and mullite present in both carbonized fluidized bed (CVFA) and its granulate (G-CVFA) are not a source of reactive aluminum for the ettringite formation process. However, an amorphous form of calcium aluminate, which could theoretically occur in the composition of amorphous fluidized matter, may constitute such a source. In this case, the ettringite formation process may proceed according to reaction (2), but the condition is high water availability.



The study of fluidized ashes placed in water, and thus with sufficient water access, did not show the presence of ettringite, probably due to the lack of reactive forms of aluminum hydroxide and/or aluminate. However, the substance $\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12}$ present in the tested sample of G-CVFA (placed in water) chemically corrodes. This is probably not a process of destruction and dissolution, but rather a conversion to new mineral phases: gypsum and hematite or iron hydroxide (goethite). This is indicated by mineralogical tests (Table 5). The reason for this process may be the presence of sulfate ions in underground mine waters and their reactions with the substance $\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12}$ according to the equations:



This also applies to the possibility of jarosite formation, which occurs in the presence of oxidized iron and sulfates in mine waters (Pluta, 1999). The above chemical reactions are important from the point of view of the possibility of using granular carbonized fly ash (G-CVFA) in underground mining techniques. It should be taken into account that due to the presence of sulfates in groundwater the possibility of fixing substances such as $\text{Ca}_6\text{Fe}_2(\text{SO}_4)_3(\text{OH})_{12}$ and $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$ or similar to ettringite might be limited, with a simultaneous increase in the amount of gypsum. This can affect the strength of the granules and requires further research.

5. Summary

Carbonation with the use of carbon dioxide seems to be a promising way to process volatile fluidized ashes, considered waste material, in order to recover and use them. Due to their physicochemical characteristics, especially the high content of free calcium, the possibility of application is very limited and sometimes even impossible.

In the light of applicable legal regulations, fluidized fly ash is not classified as hazardous waste. However, as mentioned earlier, this ash is characterized by the fact that in its composition they contain much more free calcium oxide CaO compared to ash from pulverized coal boilers. The amount of free calcium oxide CaO in this type of waste can reach up to 10 wt. or even exceed this value. In accordance with the criteria of Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (Text with EEA relevance) calcium oxide CaO is classified as an irritant and is designated H315 and H318. According to the final Commission Decision No 2000/532/EC of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste (notified under document number C(2000) 1147) (Text with EEA relevance), when the waste contains one or more substances in quantities above the limit, which are classified by one of the following hazard categories and hazard assignment codes – H314, H315, H318, H319 and if one or more of the permissible concentrations is reached or exceeded, then the waste must be classified as hazardous, with the limit to recognize that the waste is hazardous due to its irritant properties is 1.0%. This means that since the entry into force of the provisions of the European Commission Decision amending Decision 2000/532 / EC, the waste from fluidized-bed boilers containing more than 1.0 wt. CaO free calcium oxide (which is practically 100%) will have to be classified as hazardous waste.

Considering the above, research was carried out to obtain a product with a controlled content of free calcium oxide eliminating this threat.

A significant reduction of CaO, or even its complete elimination, is obtained through conversion to calcium carbonate (CaCO₃). This opens new perspectives for the application of carbonated fly fluidized ashes in various types of mining techniques. In micro aggregate, obtained through the carbonation of the fluidized fly ash, sodium carbonate and calcium sulfates are present, which are relevant to the formation and crystallization of ettringite - one of the primary factors influencing the quality of the bonding structure of the solidified fluidized ashes (Kurdowski, 2010). To what extent these components will act synergistically or competitively depends on their shares in volatile fluidized ash (its chemical composition) and the water content. A change in the ratio of calcite to anhydrite in the fluidized fly ash causes calcium sulfate connections to react differently in the processed and unprocessed ash-related products. During carbonation the quantitative relations between carbonates and sulfates change – most of all the formation of bassanite occurs, which is a precursor of gypsum crystallisation. It could be postulated that perhaps this fact will play an important role in the future directions of fluidized fly ash management as an additive in concrete (Łączny & Bzowski, 2017).

In the presented complex system of chemical reactions, sulfate connections behave in a quaint way. The compounds containing sulfate ions undergo different reactions depending on whether

the volatile fluidized ash was subjected to carbonation or not. The bassanite emerging in the tested solidified ash samples is a precursor in the gypsum crystallization process (Van Driessche, 2012).

6. Conclusions

The obtained 2-10 mm grain size class carbonated fluidised ash granulate (G-CVFA) contained 0.5% free calcium oxide, resulting in a relatively high pH of 10.5 of water extract. This is probably related to the breakdown of the grains of volatile fluidal ashes, in which free calcium oxide is encapsulated, due to hydration processes of the amorphous part of the ash grains. Almost 10% washability and crushing resistance value of 4.8 MPa may indicate that the processed free calcium oxide becomes the bonding agent of the G-CVFA granules. Relatively high water permeability ($4.8 \cdot 10^{-4}$ m/s) creates favourable conditions for the draining of the granulate used in underground excavations.

The mineral composition of the tested granulate (G-CVFA) is dominated by an amorphous substance probably containing calcium compounds prone to phase change, which confirms the presence of phase substances similar to the braunmillerite. It can be assumed that there is a relationship between the amorphous substance of the granulate and its pozzolanic properties. This thesis, however, requires verification.

The impact of both fresh (surface) water and saline groundwater (mine) on granulated carbonated fluidized ash (G-CVAF), causes the formation of a significant amount of gypsum as well as partial corrosion of the granulate.

In reaction with saline groundwater (mine), the G-CVAF material exhibits poor sorption properties, retaining halite and sulfates in the form of jarosite. This product can be used in hard coal mining in underground mining techniques because, due to it being subjected to carbonation and granulation processes, it remains stable in mine water environment.

The improvement of sorption quality by the addition of, for example, zeolites to carbonated fluidized ashes at the stage of granulation, may increase the retention of sulfate ions and activate crystallization processes in sulfate-containing substances, which should be a new direction of research.

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References

- Agusta H., Nisya F.N., Iman R.N., Bilad D.B., 2017. *Granulation of coal fly ash by using different types of granule agents*. International Conference on Biomass: Technology, Application, and Sustainable Development. IOP Conf. Series: Earth and Environmental Science **65**, 1-13.
- Albinami A., Willis B., 1982. *Journal of Applied Crystallography* **15** (4), 361-374.
- Anthony E.J., Granatstein D.L., 2001. *Progress in Energy and Combustion Science* **27**, 215-236.
- Bish D.L., Post J.E., 1993. *American Mineralogist* **78** (9-10), 932-940.
- Bogdanov B., Hristov Y., Markovska I., Rusev D., Georgiev D., 2012. *Oxidation Communication* **35** (1), 228-238.

- Van Driessche A.E.S., Benning L.G., Rodriguez-Blanco J.D., Ossorio M., Bots P., García-Ruiz J.M., 2012. *Science* **336** (6077), 69-72.
- Giergiczny E., 2007, *Popiół lotny ze współspalania jako dodatek do cementu i betonu w aspekcie wymagań normowych i środowiskowych*. XIV Międzynarodowa Konferencja Popioły z Energetyki, Międzyzdroje.
- Gomathi P., 2015. *Evaluation on the strength and durability properties of alkali activated fly ash aggregate incorporated concrete composites*. VIT University.
- Heim A., 2012. *Chemik* **66** (5), 356-359.
- Kanafek J., Łączny M.J., Róg L., 2018. *Zjawisko powstawania wodoru w ups pochodzących ze współspalania węgla i biomasy*. XXV Międzynarodowa Konferencja Popioły z Energetyki, Krynica Zdrój, 1-10.
- Klässien P.W., Griszajew I.G., 1989. *Podstawy techniki granulacji*. Inżynieria Chemiczna, WNT, Warszawa.
- Korol J., Serkowski S., 2005. *Wiadomości Hutnicze* **5**, 296-300.
- Kowalska S., 2013. *Nafta-Gaz* **69** (12), 894-902.
- Kurdowski W., 2010. *Chemia cementu i betonu*. Stowarzyszenie Producentów Cementu, Kraków; Wydawnictwo Naukowe PWN, Warszawa.
- Łączny M.J., Bzowski Z., 2017. *Journal of Sustainable Mining* **16** (4), 151-155.
- Łączny M.J., Iwaszenko S., Gogoła K., Bajerski A., Janoszek T., Klupa A., Cempa-Balewicz M., 2015. *Journal of Sustainable Mining* **14** (4), 164-172.
- Łączny M.J., Majka G., Cempa-Balewicz M., 2016. *Cement Wapno Beton* **4**, 265-273.
- Mahieux P.Y., Aubert J.E., Cyr M., Coutand M., Husson B., 2010. *Waste Manag* **30** (3), 378-388.
- Morsch U., 2005. *100 years Erich Mixing Technology (1903-2003)*. Wissensportal Baumaschine, no 1.
- Ohnaka A., Hongo T., Ohta M., Izumo Y., 2005. *Research and development of coal ash granulated material for civil engineering applications*. Conference "World of coal ash (WOCA)". USA: Lexington, Kentucky, 11-15 April, 1-8.
- PL 410867 "Method for processing volatile ashes from the use of the energy producing fuels for the product with controlled content of free calcium oxide".
- Pluta I., 1999. *Przegląd Górniczy* **7-8**, 15-18.
- Rajczyk K., 2012. *Popioły lotne z kotłów fluidalnych możliwość ich uszlachetniania*. Instytut Ceramiki i Materiałów Budowlanych, Opole.
- Stoch A., 2015. *Fly ash from coal combustion – characterization*. Dissertation, Tecnico Lisboa, 15-35.
- Szczygielski T., Tora B., Kornacki A., Hyncnar J.J., 2017. *Inżynieria Mineralna* **18** (1), 207-216.
- Wójcik M., Stachowicz F., Masłoń A., 2017. *Journal Of Civil Engineering, Environment And Architecture*, XXXIV, **64**, 377-393.